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N₂-CO₂ co-injection field test at the Ketzin pilot CO₂ storage site

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Abstract

In summer 2013, a four week N₂-CO₂ co-injection field test was conducted at the Ketzin pilot site. Major objectives were (i) demonstrating the technical feasibility of a continuous N₂-CO₂ co-injection scenario, (ii) monitoring wellhead and reservoir pressure, (iii) monitoring spreading and behavior of the CO₂-N₂ gas mixture in the reservoir, and (iv) analyzing potential chromatographic effects within the reservoir. 10,000 L (10 Nm³) of krypton (Kr) were injected as an additional conservative chemical tracer prior to injection of the N₂-CO₂ gas mixture. For the field test CO₂ from a natural CO₂ source with a much heavier carbon isotope composition ($\delta^{13}\text{C} = -3.4 \pm 0.2\text{‰}$) was injected instead of the previously used industrial CO₂ ($\delta^{13}\text{C} = -30.6 \pm 0.4\text{‰}$) from a refinery process to allow for examination of isotopic effects. Vital parameters during monitoring include N₂ and CO₂ injection rates, pressure and temperature at injection and observation wells, and reservoir pressure, respectively. A capillary riser tube was used to collect reservoir fluid and gas samples. These were analyzed for gas and carbon isotope compositions.

Preliminary results show successful realization of the N₂-CO₂ co-injection field test next to effective and permanent monitoring of the injected gases (N₂, CO₂ and Kr) and vital storage parameters (wellhead pressures, reservoir pressure and reservoir temperature). During the field test, 32 t of N₂ and 613 t of CO₂ were co-injected in total to ensure a CO₂:N₂ volume ratio of approximately 95:5. Despite some variation of both N₂ and CO₂ injection rates, wellhead pressure and reservoir pressure were well controlled during the entire field test, and thereafter. Based on $\delta^{13}\text{C}$ data, the gas mixture arrived after about 17 days at the first observation well (Ktzi 203) located at about 25 m distance to the injection well (Ktzi 201). Increasing Kr concentrations at Ktzi 203 positively correlate with both increasing N₂ concentrations and $\delta^{13}\text{C}$ values. Additionally, the $\delta^{13}\text{C}$ data also indicate mixing between natural and industrial CO₂ within the reservoir.

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Keywords: Ketzin pilot site; large-scale field test; N₂-CO₂ co-injection; monitoring

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1. Introduction

The Ketzin pilot site for geological CO₂ storage is located about 25 km west of Berlin in the federal state of Brandenburg, Germany. The site represents Europe's first and longest operating on-shore CO₂ storage facility [1], [2]. Between June 2008 and August 2013, slightly more than 67 kt of high-purity CO₂ (purity > 99.7%) were injected into a saline aquifer of the Upper Triassic Stuttgart Formation, which is situated at approximately 620 m below surface. Due to this relatively shallow depth, the site is characterized by a unique setting of concomitant low ambient P-T conditions compared to other geological CO₂ storage operations. Both R&D programs as well as the applied monitoring methods at Ketzin are amongst the most comprehensive worldwide. Accordingly, scientific investigations at Ketzin provide fundamental knowledge for geological CO₂ storage in saline aquifers and the site is recognized as a reference project for the investigation and realization of geological CO₂ storage, in general [3].

Contrary to the regular injection operation at the Ketzin site, the CO₂ stream of future industrial CO₂ storage projects will contain certain amounts of impurities, which may influence the storage operation and also the behavior of the CO₂ stream within the reservoir. To evaluate the impact of the quality of CO₂ on transport and storage behavior, field studies and experiments on semi-industrial scale have been scheduled within the EU funded collaborative IMPACTS project to study operational and material effects of impurities in CO₂ streams. Within this frame a four week N₂-CO₂ co-injection field test was performed at the Ketzin site between July 24th and August 18th 2013 to i) demonstrate the technical feasibility of a continuous N₂-CO₂ co-injection scenario, ii) monitor pressure evolution at the wellhead(s) and within the reservoir, iii) monitor spreading and behavior of the N₂-CO₂ gas mixture within the reservoir, and iv) analyze potential chromatographic effects within the reservoir. This paper presents first operational and monitoring data for this field test.

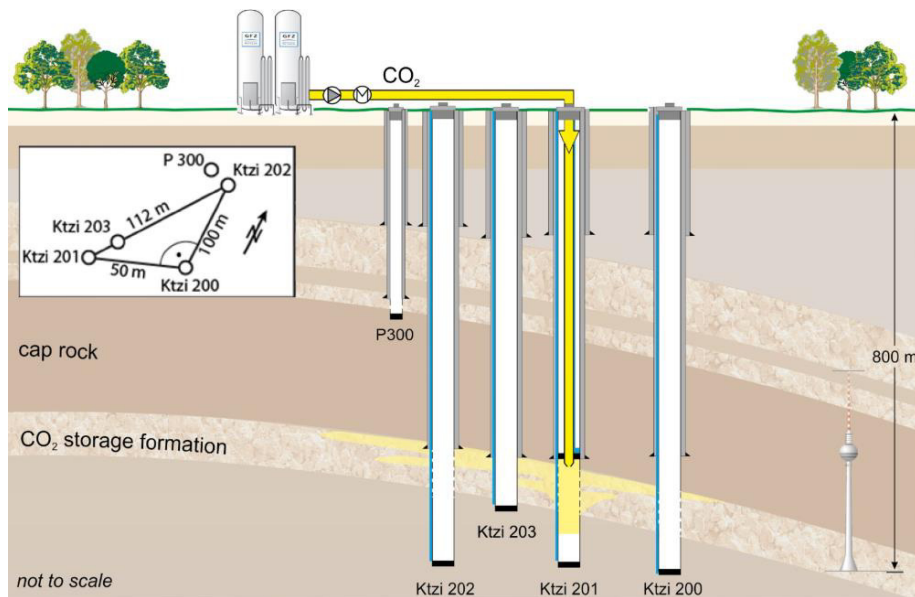


Fig. 1. Schematic image illustrating the arrangement of wells at the Ketzin site (adapted from B. Schöbel/T.Kollersberger, GFZ Potsdam).

2. Methods and Methodology

2.1. General Approach

During the four-week field test 32 t N₂ and 613 t CO₂ were co-injected resulting in an overall CO₂:N₂ volume ratio of 95:5. To ensure continuous injection, daytime surveillance of the co-injection process and to provide a specific CO₂:N₂ injection characteristic to study in-reservoir processes, the CO₂ was injected continuously for 24 h/d

throughout the entire experiment while N_2 was added to the CO_2 stream and co-injected discontinuously for 10-hour intervals each day through most of the four-week timeframe.

In order to extend the monitoring strategy, 10,000 L (10 Nm³) of krypton (Kr) were injected as an additional conservative chemical tracer prior to injection of the N_2 - CO_2 mixture. Moreover, CO_2 from a natural CO_2 source (in the following referred to as “Herste CO_2 ”) was temporarily injected during the test instead of the usually used industrial CO_2 from a refinery process (in the following referred to as “industrial” CO_2). Herste CO_2 has a much heavier carbon isotope composition ($\delta^{13}C = -3.4 \pm 0.2\text{‰}$) compared to the industrial CO_2 ($\delta^{13}C = -30.6 \pm 0.4\text{‰}$). This additionally allows for detection of potential isotopic effects due to mixing between the injected Herste CO_2 and formation brine, and previously injected industrial CO_2 .

Vital parameters during monitoring include injection rates (i.e. mass flows) of N_2 and CO_2 , pressure and temperature at the injection (Ktzi 201) and observation wells (Ktzi 200, Ktzi 202 and Ktzi 203; Fig. 1), and reservoir pressure, respectively. A capillary riser tube was used for collecting reservoir fluid and gas samples at observation well Ktzi 203. For monitoring the isotopic changes during the test, injected N_2 and CO_2 as well as reservoir gas was sampled on a daily basis with septum-sealed vials, and analyzed with a Gasbench II and DELTAplusXL IRMS. Gas compositions were determined by gas chromatography (SRI 8610 C, SRI Instruments) every 20 minutes, and by mass spectroscopy (Omnistar, Pfeiffer Vacuum), every 5 minutes, respectively. Note that Ktzi 203 is the observation well situated closest to Ktzi 201 at a distance of only 25 m.



Fig. 2. **A:** Connection hose between N_2 storage tank and high pressure N_2 pump; **B:** Connection port of the stainless steel tube to $\frac{1}{2}$ " NPT valve at Ktzi 201 wellhead; **C&D:** Stainless steel tubing between high pressure N_2 pump and Ktzi 201 wellhead (Photographs by S. Fischer).

2.2. Technical Concept

Liquid N_2 was delivered by truck and temporarily stored in a mobile storage tank (Fig. 2A) at the site close to the injection well Ktzi 201. A mobile high pressure pump was connected to the storage tank (Fig. 2A&B) and was used for N_2 injection. The high pressure pump was pressure regulated, i.e. N_2 injection was realized by setting the pressure of the N_2 stream (slightly) higher than that of the CO_2 stream. Hence, N_2 was flowing from the N_2 storage tank into the high pressure pump and from there into the Ktzi 201 wellhead where it mixed with the CO_2 stream. A stainless steel tubing was used to connect the high pressure pump to the $\frac{1}{2}$ " NPT valve at the Ktzi 201 wellhead (Fig 2C, D & E). Hand wheels at the transmission of the high pressure pump were used to adjust the injection pressure of the N_2 stream and hence control the N_2 mass flow. The actual N_2 mass flow was measured through a flow meter located at the outlet of the high pressure pump. Values of the actual N_2 mass flow were shown on and collected from a digital display at the pump station. For injection into the CO_2 stream the liquid N_2 was heated to approximately 10 °C above ambient temperature to assure injection of gaseous N_2 .

3. Results

The N_2 - CO_2 co-injection field test at the Ketzin pilot site was conducted between July 24th and August 18th 2013. In the beginning of the test it was found that N_2 rates were larger than previously intended. This was due to the N_2 pump, which was still exceeding the pre-calculated N_2 mass flow while being set to minimal stroke. The intended, continuous N_2 mass flow of 1.6 t/d could hence not be realized and it was decided to have discontinuous N_2 injection. To finally arrive at a CO_2 : N_2 volume ratio of 95:5, N_2 injection was run in 10-hour intervals daily.

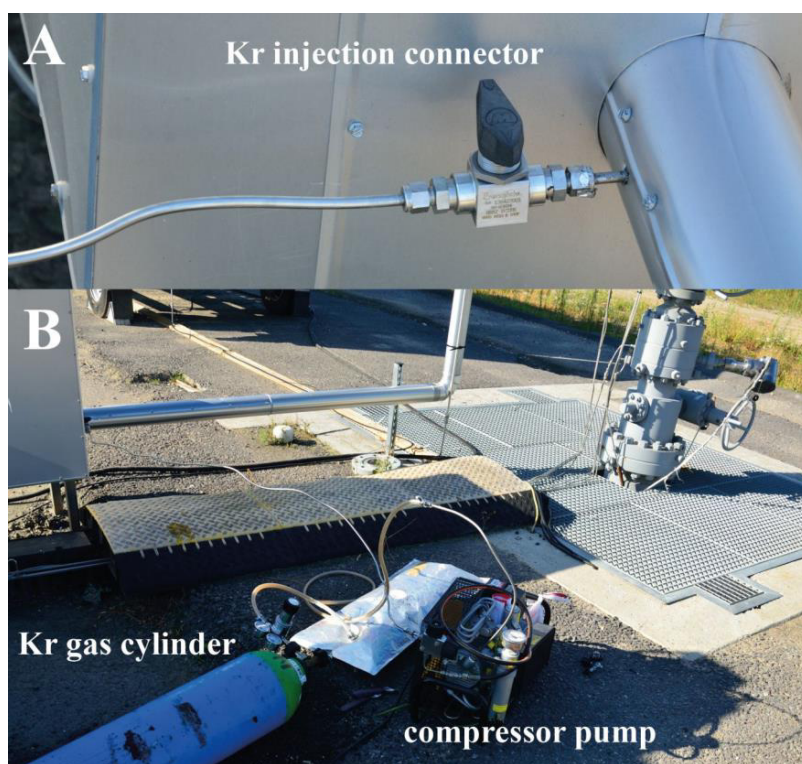


Fig. 3. Set up for the injection of the Kr tracer prior to the start of the N_2 - CO_2 co-injection test (Photographs by S. Fischer); **A:** High-pressure valve connecting the feed line from the Kr gas cylinder to the CO_2 injection pipeline; **B:** Kr gas cylinder, compressor pump and equipment used for Kr injection.

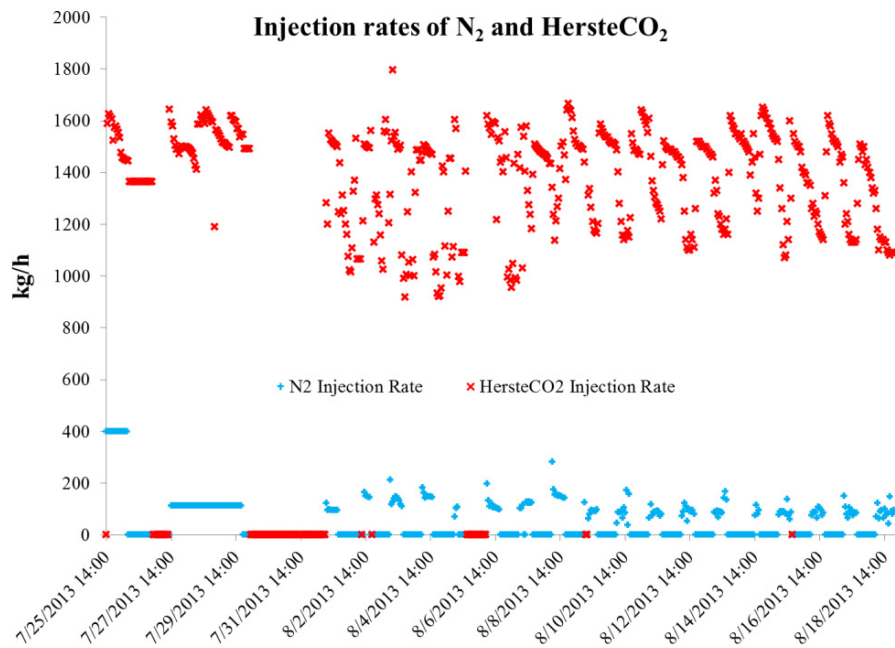


Fig. 4. Injection rate history for N_2 and Herste CO_2 as during the N_2 - CO_2 co-injection field test at Ketzin. Note that each data point for the individual rate represents a single hour value.

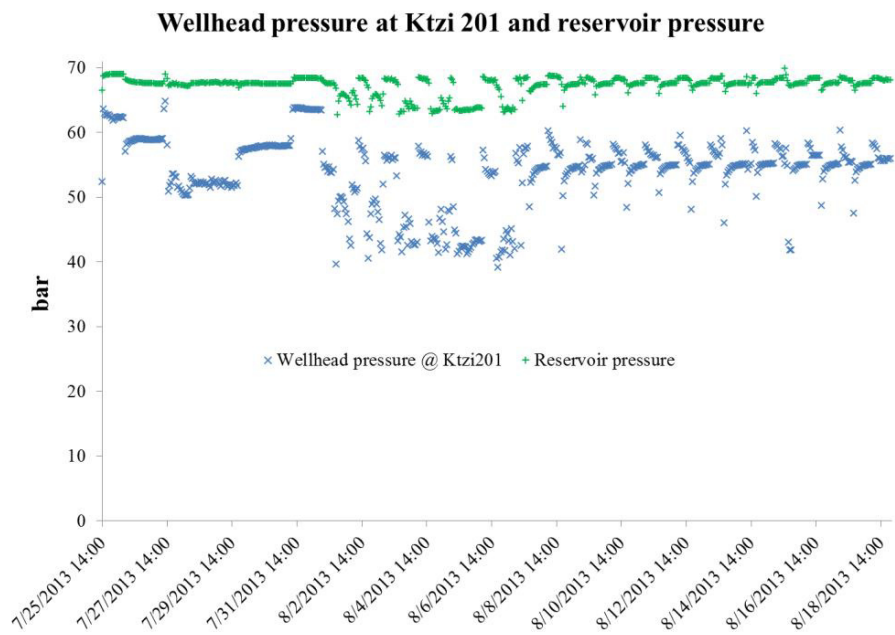


Fig. 5. History of wellhead and reservoir pressures (as measured at 550 m depth) during the N_2 - CO_2 co-injection field test at the Ketzin pilot site. Note that each data point for individual pressure represents a single hour value.

Preliminary results show successful realization of the N₂-CO₂ co-injection next to effective and permanent monitoring of the injected gases (N₂, CO₂ and Kr) and vital storage parameters (wellhead pressures, reservoir pressure and reservoir temperature). During the field test, 32 t of N₂ and 613 t of CO₂ (433 t HersteCO₂ plus 180 t industrial CO₂) were co-injected in total to ensure a CO₂:N₂ volume ratio of 95:5. The Kr tracer injection was realized by attaching a feed line from the Kr gas cylinder to a high-pressure valve located directly at the CO₂ injection pipeline (Fig. 3A). In order to inject the entire Kr volume from the gas cylinder, a compressor pump was interposed between the gas cylinder and the high-pressure valve (Fig. 3B). Note that during the four hour Kr injection process, both CO₂ as well as N₂ injection streams were stopped.

Despite some variation of both N₂ and CO₂ injection rates as shown in Figure 4, wellhead pressure, reservoir pressure (Fig. 5) and temperature of the injection well Ktzi 201, for example, were well controlled during the entire field test, and thereafter. While the injection rates for HersteCO₂ varied between 77 and 2000 kg CO₂/h, those of N₂ varied between 39 and ~200 kg N₂/h (Fig. 4). (Note that N₂ injection rates of 400 kg/h only occurred during the starting phase.) Similar to the injection rates of N₂ and CO₂ also the evolution of the wellhead pressure at Ktzi 201 and the reservoir pressure shows ups and downs. While the wellhead pressure at Ktzi 201 reveals larger variation between 39.1 and 64.8 bar, the reservoir pressure (as measured in 550 m depth at Ktzi 201) ranged from 62.7 to 69.9 bar (Fig. 5).

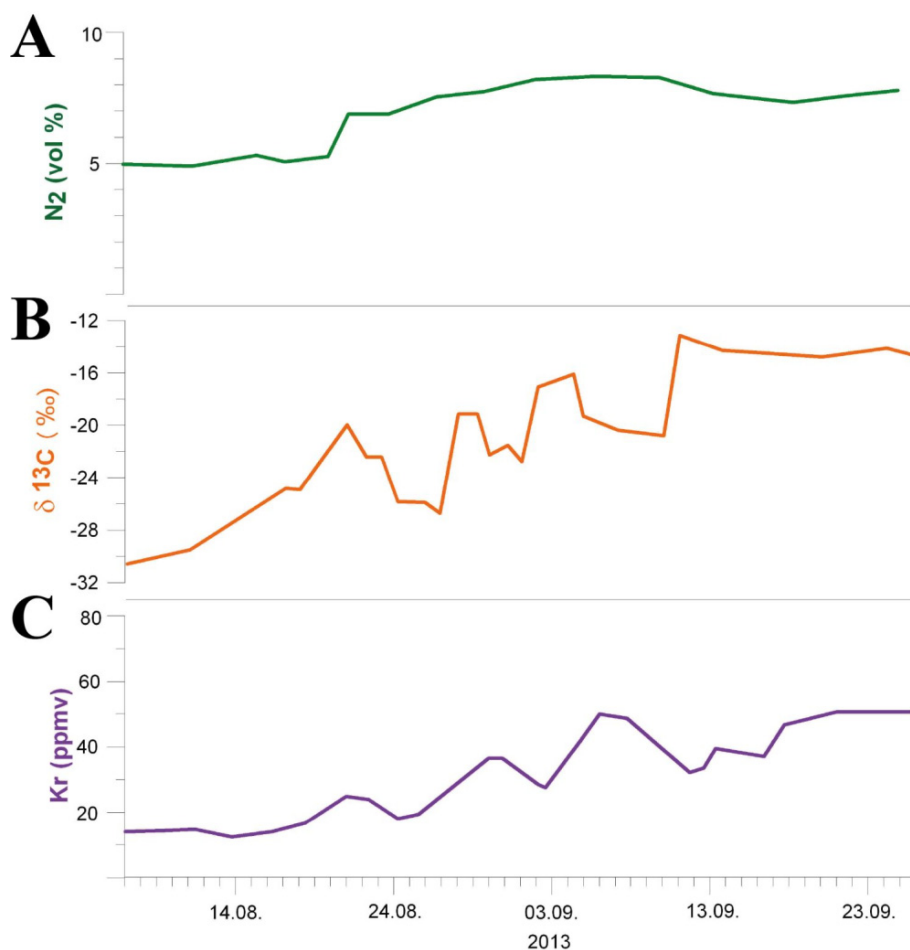


Fig. 6. Monitoring history of gas measurements at the observation well Ktzi 203 as determined during and after the N₂-CO₂ co-injection field test at the Ketzin pilot CO₂ storage site. **A:** N₂ concentrations [%]; **B:** $\delta^{13}\text{C}$ values [‰]; **C:** Kr concentrations [ppmv].

The analysis of the gas composition as determined at observation well Ktzi 203 reveals increasing N₂ and Kr concentrations, as well as a change in the isotopic composition of the injected CO₂ (Fig. 6). The onset of the isotopic changes occurred around August 11th, whereas a significant increase in N₂ and Kr concentrations is apparent after August 18th. The N₂ concentration (Fig. 6A) increases steadily from five to about eight vol% on September 10th and then stays relatively constant thereafter. The $\delta^{13}\text{C}$ value shows a similar behavior. However, in Figure 6B three periods can be distinguished during which the $\delta^{13}\text{C}$ value decreases significantly. The highest $\delta^{13}\text{C}$ value of about -14‰ was measured on September 11th. Similar to the $\delta^{13}\text{C}$ behavior also Kr concentrations (Fig. 6C) reveal (at least) three periods of significant concentration decreases before reaching a stable concentration level of about 50 ppmv around September 20th.

4. Conclusions

The N₂-CO₂ co-injection field test at the Ketzin pilot CO₂ storage site was safely performed. Both wellhead pressure at the injection well Ktzi 201 and the reservoir pressure were well controlled during the field test. Both parameters positively correlate with N₂ and HersteCO₂ injection rates. The wellhead pressure revealed larger variance compared to the reservoir pressure as it was strongly influenced by changes in the N₂ injection rate. Based on Kr data, the gas mixture arrived after about 17 days at the first observation well (Ktzi 203) located about 25 m away from the injection well (Ktzi 201). Gas chromatography and mass spectrometric measurements at Ktzi 203 furthermore show that the isotopic composition of the injected CO₂ changed during migration through the reservoir, on the one hand, and that both $\delta^{13}\text{C}$ and Kr trends are characterized by several significant increases and decreases reflecting varying N₂ (and CO₂) injection conditions, on the other. Increasing Kr concentrations at Ktzi 203 positively correlate with both increasing N₂ concentrations as well as $\delta^{13}\text{C}$ values. Apart from that positive correlation, the $\delta^{13}\text{C}$ data additionally show mixing between previously present industrial CO₂ and HersteCO₂ within the reservoir.

5. Outlook

In autumn 2014 a back-production test of CO₂ is scheduled at the Ketzin pilot site. This comprises, amongst others, the back production of approximately 1,000 t reservoir fluid, i.e. mainly CO₂-rich gas and subordinate brine. In this context it will be interesting to analyze the gas composition and determine N₂ and Kr concentrations as well as $\delta^{13}\text{C}$ values of the back-produced gas and brine as these data could offer valuable information on trapping mechanisms, retention times for individual components (impurities) in CO₂ and for gaining a better understanding of the Ketzin reservoir.

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References

- [1] Martens S, Kempka T, Liebscher A, Lüth S, Möller F, Myrntinen B, Norden B, Schmidt-Hattenberger C, Zimmer M, Kühn M. Europe's longest-operating on-shore CO₂ storage site at Ketzin, Germany: a progress report after three years of injection. *Environmental Earth Sciences* 2012; 67 (2): 323–334.
- [2] Martens S, Liebscher A, Möller F, Henningsen J, Kempka T, Lüth S, Norden B, Prevedel B, Szizybalski A, Zimmer M, Kühn M. CO₂ storage at the Ketzin pilot site, Germany: Fourth year of injection, monitoring, modelling and verification. *Energy Procedia* 2013; 37: 6434–6443.
- [3] Michael K, Golab A, Shulakova V, Ennis-King J, Allinson G, Sharma S, Aiken T. Geological storage of CO₂ in saline aquifers—A review of the experience from existing storage operations. *International Journal of Greenhouse Gas Control* 2010; 4: 659–667.